May 6, 1969 S. L. SHILLER ET AL 3,442,782

ELECTROCHEMICAL ELECTRODE

Filed May 24, 1966

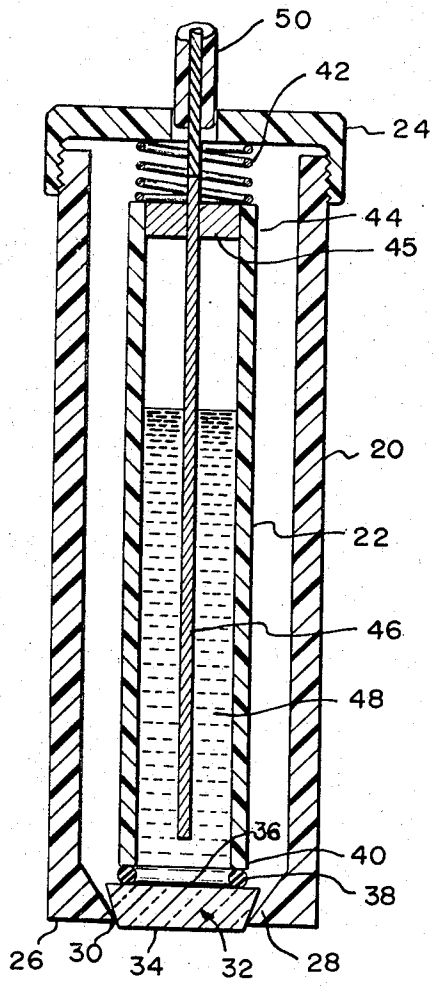


FIG. 1

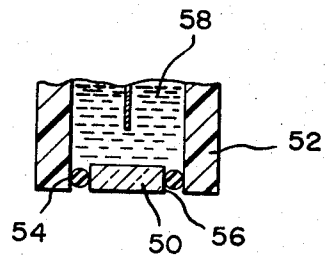


FIG. 2

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United States Patent Office 3,442,782
Patented May 6, 1969

3,442,782

ELECTROCHEMICAL ELECTRODE

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Filed May 24, 1966, Ser. No. 552,597
Int. Cl. B01k 3/12, 3/06, 3/04
U.S. Cl. 204—195 8 Claims

ABSTRACT OF THE DISCLOSURE

A potentiometric electrode structure formed of a pair of coaxial, spaced-apart cylinders of electrically insulating material. A wafer of ion-sensitive material is disposed in one open end of the outer cylinder such that the periphery of the wafer is in substantially continuous ribbon contact with the edge of the opening. The inner container is sealed to the inner surface of the wafer and is resiliently biased against the wafer so as to force it into the ribbon contact. The material of the outer container is deformable so that the pressure of the wafer against the ribbon contact creates a seal. The inner container is intended to contain an internal reference electrode and electrolyte.

This application relates to electrochemical devices and more particularly to an electrode structure for electrochemical analysis.

In the United States applications Ser. No. 511,751, filed by Martin S. Frant and James W. Ross on Dec. 6, 1965, and 525,197, filed by Martin S. Frant on Feb. 4, 1966, both assigned to the assignee of this application, there are disclosed ion-sensitive electrodes using crystalline materials as ion-sensitive membranes. Particularly, these crystalline materials are used to separate two solutions one of which contains a reference solution having a substantially fixed conceneration of the ions to which the membrane is sensitive, and the other of which is the sample solution of which the concentration or activity of the particular ion in question is to be determined. A potential E will develop across the crystalline membrane when in contact with the two solutions, the potential being in accordance with the well known Nernst equation as follows:

$$E = \text{constant} + \frac{RT}{F} \ln A \quad (1)$$

in which A is the activity of the desired ion in the sample solution. Specifically, it has been found that a membrane of a crystalline fluoride salt, highly insoluble in aqueous solution, when separating two solutions, one of which is a reference solution and the other of which is the sample solution, will provide a Nernstian potential corresponding to the fluoride ion activity in the sample solution. Examples of such salts are a number of the rare-earth metal fluorides such as LaF_3, CeF_3, PrF_3, NdF_3, and others such as BiF_3, and PbF_2. Similarly, sulfide ion activity can be determined, particularly by using very pure Ag_2S membranes. These crystalline materials not only need to be highly insoluble but should be substantially imporous. For example, the rare earth trifluorides typically are used as massive monocrystals; where the membrane crystal can be grown, if at all, with great difficulty, a highly compressed polycrystalline membrane can be formed instead, typically as in the case of Ag_2S.

All of these crystalline membranes exhibit fairly large bulk resistivities (ca. 10^8 ohm-cm.) Consequently, the potential developed across the crystal membrane is determined with the usual high input impedance electrometer such as a vacuum tube voltmeter.

In constructing electrodes using these crystalline ion-sensitive membranes, it is necessary to insure that no low impedance paths exist between the internal reference solution and the sample solution, otherwise the voltage developed, at best will be drifty, and certainly will be inaccurate.

Typically, such electrodes are formed using a very highly electrically resistive glass or synthetic polymeric tube as the container for the internal reference electrolyte, the membrane being sealed across an end of the tube in contact with the reference electrolyte. The usual sealing methods have not been very satisfactory in providing leakage-free seals. Typically, a number of epoxy resins, polyester resins, waxes, etc., have been found to be quite unsatisfactory in that they do not bind properly to the crystal itself, or permit aqueous leakage at the crystal-sealant interface.

In addition, it is important that no grooves or other depressions be formed adjacent to the crystalline surface as these provide minute traps for sample solutions. When the electrode is placed into another sample solution having a different ionic activity, the trapped portion of the previous sample tends to provide a spurious reading, or at least cause the electrode potential to drift until the trapped solution diffuses out or is mixed with the new sample solution.

It is, therefore, a principal object of the present invention to provide an improved electrode assembly employing crystalline ion-sensitive membranes, which electrode assembly is substantially free of the foregoing problems in that the crystalline seal is substantially electrically leak free and a minimum of surface irregularities exist adjacent the crystalline material.

Other objects of the invention will in part be obvious and will in part appear hereinafter. The invention accordingly comprises the apparatus possessing the construction, combination of elements, and arrangement of parts which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. 1 is an elevated schematic view of a section through an electrode embodying the principles of the present invention; and

FIG. 2 is a schematic section through a portion of an electrode of the prior art illustrating one of the problems outlined above.

Referring now to FIG. 1 there will be seen an embodiment of the electrode structure of the present invention including means for containing a body of reference electrolytic fluid and comprising preferably a double-walled container formed of outer shell **20** and inner tube **22**. Preferably shell **20** and tube **22** are hollow cylinders and are coaxial with one another, shell **20** being larger in diameter and longer than tube **22**. Both tube **22** and shell **20** are preferably both formed of a high electrical resistance, substantially chemically inert material (at least to the electrolytes involved) such as polyvinyl chloride, polytetrafluoroethylene or the like, which is preferably deformable under pressure. One end of shell **20** is covered with a threaded, centrally apertured cap **24**. Adjacent other end **26** of shell **20** is an internally conically tapered lip **28** arranged so that the opening at end **26** is reduced, i.e., of lesser diameter than the internal diameter of the remainder of the shell. End **26** of shell **20** is substantially flat, i.e., a cross-sectional plane, so that the latter, intersecting the internal conical taper of lip **28**, forms sharp edge **30** at the periphery of the opening at end **26**.

Disposed within the opening of shell **20** at end **26** is crystalline, ion-sensitive membrane **32** of the type hereinbefore described, preferably formed in a frustoconical shape, i.e., the part of an isoceles conical solid formed by cutting off the top of a cone with a plane parallel to the plane of the base. Membrane **32** is disposed such that the smaller area planar surface **34** thereof extends outwardly from the opening in shell **20** beyond the plane of end **26**, the larger area planar surface **36** being therefore disposed within the interior of the shell. It will be seen then that edge **26** continually contacts the conical periphery of membrane **32**, preferably along an intersecting circular line lying in a plane parallel to the planes of surfaces **34** and **36**. The solid conical angle of membrane **32** is preferably less (i.e., more acute) than the conical angle of the taper of lip **28**.

Tube **22** which is of lesser internal diameter than the diameter of surface **36**, is positioned so that one end **40** of the tube bears against O-ring **38** of like diameter, the O-ring being disposed on and concentric with surface **36**. O-ring **38**, which is preferably elastically deformable by lesser pressure than that which would unduly stress membrane **32**, and which is formed of electrically insulating material, such as polytetrafluoroethylene, hence comprises means for sealing end **40** of tube **22** to surface **36**.

Tube **22** is held against O-ring **38** by pressure exerted by resilient means such as spring **42**, the latter being maintained in compression between cap **24** and opposite end **44** of tube **22**. Thus, the O-ring not only serves as a seal but more importantly tends to distribute the pressure of tube **22** more widely over surface **36** of membrane **32**, thus minimizing the possibility of fracture of the crystal by stresses which might occur due to irregularities in the edge of end **40** of tube **22**.

Positioned within tube **22** and extending preferably from a position adjacent end **40** (but not touching surface **36**) to and through seal or plug **45** in opposite end **44** of the tube, is electrically conductive reference electrode **46**, usually of a metal and a salt thereof selected according to the nature of the ion to be measured. Thus, as shown, plug **45**, tube **22**, O-ring **38** and surface **36** form a sealed enclosure in which is disposed a body of reference electrolyte **48** in contact with both surface **36** and electrode **44**. Electrode **46** is connected to the usual coaxial cable **50** which preferably extends through the central aperture of the cap.

Typically, where membrane **32** is a rare-earth metal fluoride, electrode **46** can be a silver-silver chloride electrode and electrolyte **48** can be an aqueous solution with fixed fluoride and silver levels, e.g., 1 N KF and 1 N KCl saturated with AgCl. Other typical electrode-electrolyte materials, depending on the nature of the membrane, are described in the above-noted applications or will be obvious to those skilled in the art.

Now it will be seen that because membrane **32** is held under the bias of spring in contact with edge **30**, and because shell **20** (at least adjacent edge **30**) is compliant, the line-contact between the membrane and shell edge tends to become a ribbon contact and form an excellent pressure seal without exerting any undue stresses on the less compliant or more brittle crystalline structure of the membrane. Because the structure of the electrode is double-walled, the seal formed between membrane and shell edge lies at the internal surface of the interspace between the tube and shell and therefore is not exposed to internal electrolyte unless fluid leakage should occur at the seal provided by O-ring **38**. Ordinarily, the double-seal arrangement insures that no low electrical impedance path will occur between reference electrolyte **48** and a sample solution contacting surface **34**. To this end, one can fill the interspace with a silicone fluid or other material immiscible with water and unreactive with either of the reference or sample solutions.

Of equal importance are the facts that the junction between the conical periphery of the membrane and end **26** is a substantially open, obtuse angle, and that both end **26** and surface **34** are substantially planar. Being readily drained, this shape will not tend to hold or trap sample fluid when the electrode is removed from a solution. For example, referring to FIG. 2 there is shown a typical prior art structure comprising a cylindircal membrane **50** held within shell **52** by a press fit into O-ring seal **54**, thereby forming an end of an enclosure for reference electrolyte fluid **58**. It will be apparent that O-ring seal **54** forms at least one annular groove **56** immediately around the edge of membrane **50**. Such grooves have been found to trap sample solution, as by capillarity. When such an assembly is transferred from one sample solution to a different sample solution in a series of measurements, the trapped fluid in groove **56** interferes seriously with the subsequent measurement.

Although the embodiment shown has been described as comprising elements of circular cross section, this is not to be construed as a limitation inasmuch as other cross-sectional configurations are useful if not as easy to manufacture.

Since certain changes may be made in the above apparatus without departing from the scope of the invention herein involved it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. In an electrochemical electrode assembly comprising, in combination,

a substantially rigid, imporous ion-sensitive membrane;

a hollow container of electrically resistive material and having an end integral therewith defining an opening, said membrane being disposed in said opening such that the entire periphery of the latter is in continuous ribbon contact with the edge surface of said membrane, at least said periphery being more deformable under pressure than said membrane; and

means resiliently biasing said membrane into said contact so as to deform said periphery to form said ribbon contact and seal said membrane within said opening.

2. In an electrochemical electrode assembly as defined in claim **1** including a second hollow container of electrically resistive material disposed within and spaced from said first container, said second container having an opening therein; and

means sealing said opening to the surface of said membrane facing inwardly of said first-mentioned container.

3. In an electrochemical electrode assembly as defined in claim **2** wherein said means for resiliently biasing said membrane comprises spring means disposed for urging said second container toward the membrane.

4. In an electrochemical electrode assembly as defined in claim **2** including a reference electrode positioned within said second container.

5. In an electrochemical electrode assembly as defined in claim **4** including a reference electrolyte solution disposed within said second container so as to provide the only electrically conductive path between said reference electrode and said surface of said membrane.

6. In an electrochemical electrode assembly as defined in claim **1** wherein said first-mentioned container is a substantially cylindrical elongated element and said end has an internally, substantially conically tapered lip terminating at said opening as a substantially circular aperture of reduced diameter in a substantially planar surface disposed diametrically across the longitudinal axis of said element so as to form a sharp, acutely angled edge around said aperture, and

wherein said membrane is substantially a frustoconical element the solid conical angle of which is more acute than the conical taper of said lip, said membrane be-

ing disposed in said aperture such that said edge is in continuous contact with the conical surface which constitutes the edge surface of said membrane;

the base plane of the frustoconical element being disposed within said first-mentioned container.

7. In an electrochemical electrode assembly as defined in claim 6 including a second hollow cylindrical container disposed within and spaced coaxially from said first mentioned container, said second container having an end opening therein; and

a pressure deformable O-ring disposed on said base plane of said frustoconical element between the latter and the periphery of the opening in said second container;

and means for biasing said second container against said O-ring.

8. In an electrochemical electrode assembly as defined in claim 7 including;

a reference electrode disposed within said second container and spaced from the latter and from said base plane, and

a body of reference electrolyte solution within said second container and in contact with both said reference electrode and said membrane.

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U.S. Cl. X.R.

204—280, 286, 295